

III.B.2 Diesel Reforming for Solid Oxide Fuel Cell Auxiliary Power Units

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Objectives

- Research and develop technologies for cost-effective and durable onboard diesel reformers for solid oxide fuel cell (SOFC) auxiliary power unit (APU) applications
- Examine experimentally the fundamentals of the diesel reforming process
 - Characterize the key parameters of the diesel reforming process
 - Fuel vaporization and mixing
 - SOFC anode exhaust recycle for water availability
 - Determine the factors that limit durability
 - Catalyst sintering and deactivation
 - Carbon formation during operation and startup
 - Develop and test processes to extend durability
 - Catalyst regeneration
- Develop models to provide a design and operation basis for a durable diesel reformer
 - Carbon formation models
 - System models to evaluate SOFC anode exhaust recycle

Approach

- Experimental measurements of diesel reforming in an adiabatic reactor
 - Simulate real-world diesel reformer operation and identify commercial design issues
 - Investigate and develop direct fuel injection and gas mixing
 - Evaluate the use of SOFC anode exhaust recycle on reactor operation, temperature profiles, carbon formation, and catalyst durability
 - Examine effects of fuel composition on operating parameters, outlet composition, and carbon formation
- Experimental measurements in an isothermal microscale reactor
 - Develop kinetic rate expression for carbon formation
 - Evaluate catalyst activity and develop rate expressions for diesel reforming
- Chemical models to interpret and codify experimental results
 - Develop chemical equilibrium model of carbon formation
 - Model reformer operation with SOFC anode exhaust recycle
 - Develop and apply kinetic models to describe details of diesel reforming process

Accomplishments

- Measured carbon formation
 - During isothermal diesel reforming simulating SOFC anode exhaust recycle
 - During adiabatic diesel reforming with anode exhaust recycle
 - Post-characterization of carbonaceous materials
- Measured catalyst surface area reduction during reforming of diesel fuel(s)
 - Measured radial and axial profiles of catalyst surface area after operation
- Measured axial temperature profiles for various operating conditions during adiabatic reforming of diesel fuel
- Measured diesel reforming characteristics simulating SOFC anode exhaust recycle
 - High adiabatic temperatures ($>800^{\circ}\text{C}$) at low recycle rates (20%)
 - Increasing recycle rates moves oxidation downstream in reformer
- Refined carbon formation model to solve issues with convergence and user interface

Future Directions

- Experimental Measurements and Process Developments
 - Carbon formation
 - Quantify as a function of catalyst and recycle ratio
 - Define diesel components that contribute to high carbon formation rates
 - Examine additive effects (e.g., ethanol) on carbon formation
 - Investigate stand-alone startup and processes to avoid carbon formation
 - Develop carbon removal/catalyst regeneration processes
 - Catalyst sintering and deactivation
 - Develop reformer operational profiles that reduce catalyst sintering
 - Stabilize active catalyst particles
 - Reformer durability and hydrocarbon breakthrough effect on SOFC
 - Incorporate SOFC ‘button’ cell operating on reformat
 - Examine sulfur effect on reforming kinetics and carbon formation
- Modeling
 - Refine carbon formation models
 - Improve model by incorporating user carbon enthalpies
 - Develop ‘user-friendly’ interface
 - Examine system effects of anode recycle such as efficiency and parasitic losses
- Technology Transfer
 - Disseminate results via publications and presentations
 - Make carbon formation model available for Solid State Energy Conversion Alliance (SECA) teams

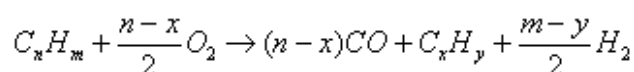
Introduction

The use of a solid oxide fuel cell (SOFC) to provide auxiliary power for diesel trucks can increase fuel efficiency and reduce emissions by reducing

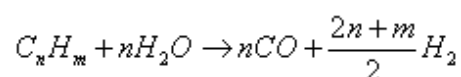
diesel engine idling time. The potential high-volume market for a SOFC auxiliary power unit (APU) could provide the driver for high-volume manufacturing to reduce the cost of a SOFC module, a key goal of the SECA Program. The logical fuel of choice for a

diesel truck SOFC APU is diesel fuel. SOFCs are being researched that directly oxidize hydrocarbon fuels, but the power densities are lower than SOFCs that use the products of reforming diesel fuel: H_2 , CO , CO_2 , H_2O , N_2 , and hydrocarbons such as methane. Since the SOFC is the costly component of the system, increasing the power density provides benefits in reducing volume, mass, and cost that can offset the cost and complexity of adding a diesel reformer to the system. The objective of this project is to research and develop the technology to enable that diesel reformer to be cost-effective and durable.

Diesel fuel can be reformed into a H_2/CO -rich fuel feed stream for a SOFC by autothermal reforming (ATR), a combination of partial oxidation (POx),



and steam reforming (SR),



The typical autothermal reformer is an adiabatic, heterogeneous catalytic reactor, and the challenges in its design and operation, particularly durable operation, on diesel fuel are manifold. These challenges begin with the vaporization and mixing of diesel fuel with air and steam where pyrolysis can occur and improper mixing leads to hot spots and incomplete conversion. Changes in diesel fuel composition such as seasonal changes affect the reactor residence time for complete conversion and the optimal operating conditions. Carbon formation during operation and startup can lead to catalyst deactivation and fouling of downstream components, reducing durability. The exotherm of the POx reaction can generate temperatures in excess of 800°C [1], where catalysts rapidly sinter, reducing their lifetime. This exothermic temperature rise can be reduced by the endotherm of steam reforming, but this requires the addition of water along with design to balance the kinetic rates. Water addition also helps to reduce carbon formation, so a key issue becomes the source of the water onboard the vehicle. Our research begins to address these issues through an experimental and modeling examination of the fundamentals of these processes. The intent is to

provide a design and operation basis for a durable diesel reformer for a SOFC APU.

Approach

Our approach is to develop a fundamental understanding of the parameters that affect the design, operation, and durability of an onboard diesel fuel reformer for a SOFC APU. We employ experimental measurements in diesel reformer reactors and microscale reactors along with development and application of chemical models to interpret and codify experimental results. Experimental measurements of diesel reforming are made in an adiabatic heterogeneous catalytic reactor to simulate real-world diesel reformer operation and to identify commercial design issues. The reactor was used to investigate and develop direct diesel fuel injection for effective fuel vaporization and mixing with air and steam. The reactor was instrumented to measure axial profiles through the catalyst volume for examination of the effects of fuel constituents on reactor performance, catalyst surface area as a function of time and temperature, and the effects of SOFC anode recycle. Carbon formation was mapped as a function of operating conditions (S/C, O/C) and quantity of SOFC anode recycle. Following the experiments, the catalyst surface area was measured using Branauer-Emmett-Teller (BET) surface area measurement and carbonaceous deposits were characterized with thermogravimetric analysis.

Experiments conducted in the adiabatic reactor were complemented by experiments conducted in a well-controlled and well-defined isothermal microscale reactor, which can be used for measurements of kinetics of diesel reforming. The isothermal experiments were used to measure carbon formation rates for both partial oxidation and steam reforming conditions over a range of temperatures.

We are developing models of the diesel reforming process and system. An equilibrium chemical code has been developed and is being further refined to model the equilibrium conditions for carbon formation as a function of operating conditions, fuel composition, and thermodynamics of deposited carbon species. The equilibrium model was expanded to model the effect of SOFC anode recycle on the diesel reformer outlet composition and

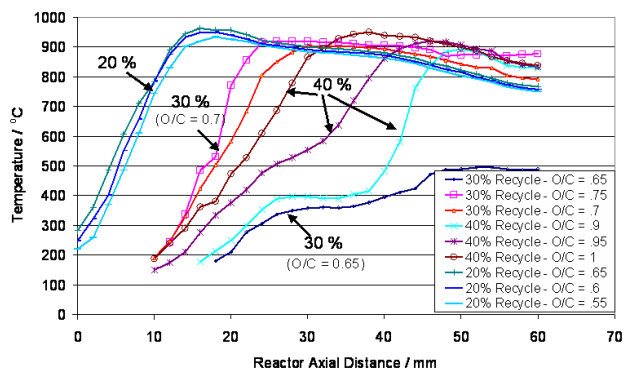


Figure 1. Axial temperature profiles measured during diesel reforming for simulated anode exhaust recycle ratios of 20% (O/C = 0.55, 0.60, 0.65), 30% (O/C = 0.65, 0.70, 0.75) and 40% (O/C = 0.90, 0.95, 1.00). Adjusted O/C with recycle ratio to obtain similar operating temperatures. Fuel was low-S Swedish diesel fuel. Pt/Rh supported catalyst, 1.5" diameter. Residence time ~ 50 msec.

temperatures. These models serve as a beginning for development of kinetic models to more accurately describe the measured temperature profiles and the diesel reforming process and to serve as a basis for optimal design of diesel reformers.

Results

A key factor in the successful operation of a commercial or experimental diesel reformer is effective vaporization of the diesel fuel and its mixing with air and steam. The challenge arises because of the propensity of diesel fuel to pyrolyze upon vaporization. This problem was solved in the experimental adiabatic reactor by using direct fuel injection through a commercial (BETE PJ8) nozzle. The air, steam, and SOFC anode recycle components were injected through an annulus around the fuel nozzle. Good mixing of the fuel and air streams was verified by thermal imaging of the outlet catalyst face. Good fuel distribution was observed at flow rates greater than 24 g/min fuel flow. Thus, the fuel turndown is limited by the flow distribution from the nozzle. Fuel/steam/air preheat was limited to below 180°C to prevent either clogging of the fuel nozzle by pyrolysis or unsteady fuel flow caused by vapor lock. The adiabatic reactor was modified further to measure axial temperature profiles through the catalyst volume

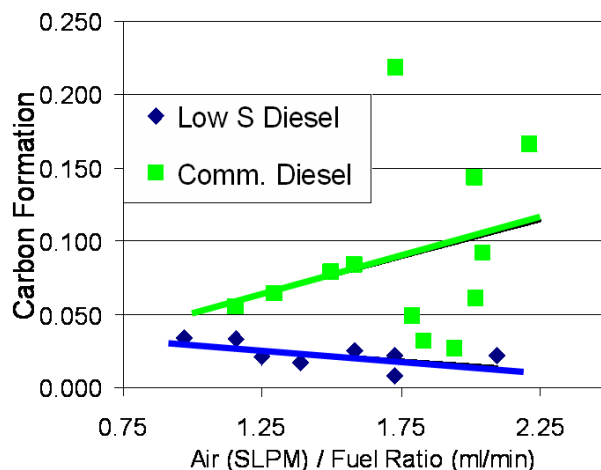


Figure 2. Carbon formation as a function of air/fuel ratio measured during adiabatic diesel reforming at 35% SOFC anode exhaust recycle ratio.

during operation. The catalysts used were Pt/Rh supported on an yttria-stabilized zirconia (YSZ) reticulated foam. This configuration of the adiabatic reactor was used in the following experiments.

Recycle of the SOFC anode exhaust into the diesel reformer is a simple method to supply water for steam reforming without an external water supply. The effect of SOFC anode exhaust recycle on diesel reforming was investigated by injecting a $H_2/N_2/H_2O$ mixture into the operating adiabatic reactor. This mixture simulates SOFC anode exhaust by substituting H_2 for the H_2 and CO content of a real exhaust and N_2 for the N_2 and CO_2 content. Figure 1 shows axial temperature profiles measured through a Pt/Rh-supported catalyst in diesel reforming of low-sulfur Swedish diesel fuel for simulated SOFC anode exhaust recycle rates of 20%, 30%, and 40%. The oxygen to carbon ratio (O/C) was increased as the recycle flow was increased in order to maintain the reformer outlet temperatures between 750 and 850°C. The temperature profiles for 20% recycle show the temperature rise from the oxidation reactions starting at the catalyst inlet and peaking about 10 mm downstream. The temperature profiles for 30% and 40% recycle rates show the temperature rise from oxidation moves downstream to about 10-20 mm from the catalyst inlet. Higher recycle ratios require an increase in the O/C to achieve a similar adiabatic temperature because of the increased flow of inert species.

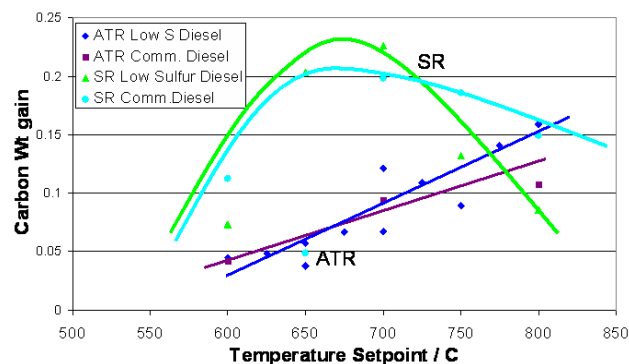


Figure 3. Carbon formation measured as a function of temperature in the isothermal microcatalyst reactor for ATR conditions ($O/C = 1.0$, $S/C = 0.34$) simulating 35% SOFC anode exhaust recycle ratio and for steam reforming conditions ($O/C = 0.0$, $S/C = 1.0$).

Experiments were conducted using the adiabatic reactor to investigate the effect of fuels and, for each fuel, to map the outlet gas composition and carbon formation as a function of operating condition. Figure 2 shows measured carbon formation in adiabatic diesel reforming of low-S Swedish diesel fuel and commercial diesel fuel as a function of air-fuel ratio. Carbon formation with the commercial diesel fuel was on average three times higher than that for the low-S Swedish diesel fuel. Carbon formation increased with increasing air flow and temperature for commercial diesel fuel, while carbon formation decreased with increasing air flow and temperature for low-S Swedish diesel fuel.

Experiments were conducted using an isothermal microscale reactor to clarify the effects of temperature and specific operating conditions on carbon formation rates. Figure 3 shows carbon formation as a function of temperature for autothermal reforming (ATR) ($O/C = 1.0$, $S/C = 0.34$) and for pure steam reforming ($O/C = 0.0$, $S/C = 1.0$) of low-S Swedish diesel fuel and commercial diesel fuel. These measurements were taken over a period of 5 hours in the microscale reactor held at a constant temperature in a tube furnace. The ATR conditions simulate similar adiabatic measurements for a SOFC anode recycle of 35%. Under these ATR conditions, carbon formation increases linearly with temperature, contrary to equilibrium predictions.

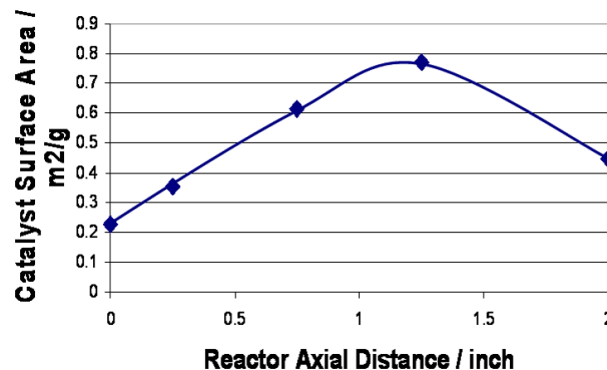


Figure 4. Axial profile of catalyst surface area (radially averaged) after adiabatic diesel reforming at 35% anode recycle by BET.

Carbon formation in steam reforming conditions appears to be limited by kinetic rates as the temperature increases to a carbon formation maximum at 700°C; then, at higher temperatures, carbon formation decreases with increasing temperature as predicted by equilibrium. In these experiments, the carbon formed during reforming was collected downstream of the catalyst and did not adhere to the Pt/Rh catalyst surface. However, carbon has been observed on the surface of Pt/Al₂O₃ catalysts in other diesel reforming measurements [10].

For a SOFC APU, a diesel reformer should convert all of the hydrocarbons in the fuel to CO, CO₂, and CH₄. In practice, hydrocarbon breakthrough is observed after 500 to 1000 hours of operation and is ascribed to loss of catalyst surface area [2,3]. A cylindrical catalyst used in the adiabatic reformer for diesel reforming measurements at a simulated anode recycle rate of 35% was sectioned axially and radially, and the catalyst surface area of each section was measured using BET. Table 1 lists the measured catalyst surface areas and the percentage remaining of the fresh surface area of ~ 4.3 m²/g. The axial profile (radially averaged) of the catalyst surface area after testing is shown in Figure 4. Catalyst surface areas are approximately constant across the catalyst but are smaller at the inlet than at longer axial distances. This is an indication that the high temperatures observed from the oxidation reaction could be sintering the catalyst at the reactor inlet.

Table 1. Catalyst surface areas measured at radial and axial locations of a Pt/Rh catalyst on a cylindrical YSZ foam support after adiabatic diesel reforming experiments with a simulated SOFC anode exhaust recycle rate of 35%. Surface areas were measured with BET. Table entries are formatted as surface area in m²/g (percent remaining of the average fresh catalyst surface area of 4.3 m²/g).

	Radius (inch)				
Depth (inch)	-0.56	-0.28	0.00	0.28	0.56
0.00	0.208 (4.8)	0.274 (6.4)	0.284 (6.6)	0.259 (6.0)	0.168 (3.9)
0.25	0.200 (4.6)	0.447 (10.4)	0.290 (6.7)	0.466 (10.8)	0.460 (10.7)
0.75	0.435 (10.1)	0.756 (17.6)	0.582 (13.5)	0.538 (12.5)	0.764 (17.8)
1.25	0.575 (13.4)	0.913 (21.2)	0.800 (18.6)	0.837 (19.5)	0.727 (16.9)
2.00	0.578 (13.4)	0.398 (9.3)	0.586 (13.6)	0.304 (7.1)	0.363 (8.4)

Conclusions

Diesel fuel reforming has been conducted under isothermal conditions and under adiabatic conditions to examine the oxidation and reforming reactions, operational conditions, catalyst activity and durability, and carbon formation. Carbon formation has been modeled for equilibrium conditions and has been measured during isothermal and adiabatic diesel reforming operation.

Diesel reforming with adiabatic operation has simulated SOFC anode recycle, without other additional water, with operation at about 30-40% recycle reasonably successful in terms of diesel conversion, carbon formation and catalyst temperature control. Temperature profiles inside the catalyst have been measured for a number of recycle rates and oxygen/carbon ratios and for various fuels, including commercial diesel and low-sulfur diesel. Increasing recycle rates moves oxidation downstream in the reformer, as does commercial diesel fuel compared with low-sulfur diesel fuel. High adiabatic temperatures (>800°C) are generally

observed at low recycle rates (20%). Operation with 30-40% recycle rate appears to be a good trade-off between high adiabatic temperatures and larger reactor volume.

Isothermal carbon formation measurements from steam reforming (O/C = 0.0, S/C = 1.0) appear to show both kinetic and equilibrium effects, with a maximum amount of carbon formation at about 700°C, for both commercial diesel fuel and low-sulfur diesel fuel. Autothermal reforming (O/C = 1.0, S/C = 0.36) measurements made isothermally show increasing carbon formation with increasing temperature, in contrast to equilibrium predictions. Adiabatic operation shows lower carbon formation for higher operating temperatures for low-sulfur diesel fuel, but higher carbon formation for higher operating temperatures for commercial diesel fuel.

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2. Fuel Composition Effect on Fuel Cell Reformer Performance and Light-off, Rodney L. Borup, Michael A. Inbody, José I. Tafoya, Troy A. Semelsberger, Will J. Vigil, and Dennis R. Guidry, 224th National Meeting of the American Chemical Society, August 20, 2003
3. Hydrocarbon Reforming for Fuel Cell Systems: Fuel Effects on Fuel Processor and Light-off, Rodney L. Borup, Michael A. Inbody, José I. Tafoya, Will J. Vigil and Dennis R. Guidry, National Meeting of the American Institute of Chemical Engineers, San Francisco, November 17-19, 2003
4. Fuels Testing in Fuel Reformers for Transportation Fuel Cells, Rodney L. Borup, Michael A. Inbody, José I. Tafoya, Troy A. Semelsberger, Will J. Vigil, and Dennis R. Guidry, 2003 SAE Powertrain & Fluid Systems Conference, Pittsburgh, October 27-30, 2003
5. Fuels Testing in Fuel Reformers for Transportation Fuel Cells, Rodney L. Borup, Michael A. Inbody, José I. Tafoya, William J. Vigil, and Troy A. Semelsberger, SAE International Paper #: 03FFL-253
6. Diesel Reforming with SOFC Anode Recycle, Rodney L. Borup, W. Jerry Parkinson, Michael A. Inbody, José I. Tafoya, and Dennis R. Guidry, Electrochemical Society, San Antonio, May 9-14, 2004
7. SOFC Anode Recycle Effect on Diesel Reforming, Rodney L. Borup, W. Jerry Parkinson, Michael A. Inbody, José I. Tafoya, and Dennis R. Guidry, American Institute of Chemical Engineers, New Orleans, April 26-29, 2004.